Quantum Mechanical Theory of Collisional Recombination Rates

William H. Miller

Department of Chemistry, University of California, and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

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Quantum mechanical expressions for the pressure-dependent recombination rate (within the strong collision assumption) are presented which have a very similar form to those developed recently for rate constants of chemical reactions: eqs 11 and 12 express the recombination rate in terms of a flux autocorrelation function, and eqs 14-16 in terms of a cumulative recombination probability. The qualitative behavior of these functions is illustrated by several pedagogical examples.

There has recently been a rebirth of interest in the theory of collisional recombination reactions1-4

\[ A + B + M \rightarrow AB + M \]  

due in part to the importance of such processes in modeling combustion3,4 (e.g., H + CO → HCO, H + O₂ → HO₂). The purpose of this paper is to present alternate quantum mechanical expressions for the recombination rate that may be more useful than existing ones for carrying out practical calculations.

The standard framework for treating recombination is the Lindemann mechanism:5

\[ A + B \leftrightarrow AB^* \]  

\[ AB^* + M \rightarrow AB + M \]  

where AB* is a metastable collision intermediate and M is an inert gas species that deactivates AB* to the recombined species AB. Within the strong collision approximation6 eq 2b is characterized only by the frequency of strong collisions, \( \omega = k_{\text{deac}}[M] \), which is proportional to the pressure of the bath gas M (where \( k_{\text{deac}} \) is the bimolecular rate constant for the deactivation step). The standard expression for the recombination rate is obtained by applying the steady-state approximation to reaction 2,

\[ k_r \equiv k_r(T,\omega) = Q_r(T)^{-1} \sum_i \exp(-\beta E_i) k_i \omega / (k_i + \omega) \]  

where \{E_i\} and \{k_i\} are the energies and unimolecular decay rates of the metastable states of AB*, \( \beta = (kT)^{-1} \), and \( Q_r \) is the reactant (A + B) partition function per unit volume. (The RRKM expression results by taking the continuum limit of eq 3, \( \Sigma \rightarrow \int dE Q(E) \), and approximating the unimolecular decay rates by microcanonical transition state theory, \( k_i \rightarrow k(E) \).)6

Classical Mechanics

I start with a dynamical expression for the recombination rate based on classical mechanics, essentially what one would do in a classical trajectory simulation.1 (It is equivalent to the classical expression for the rate given by Slater.)7 Once the classical expressions are written appropriately, their quantization will be apparent.

Referring to Figure 1 (a schematic of the A + B potential energy surface), the recombination rate is the Boltzmann average of the flux of trajectories into the complex region (\( r < a \) which

\[ F = -\frac{d}{dr} h[-f(q)] = \delta[f(q)] \frac{df}{dq} \cdot (p/m) \]  

The minus sign in eq 4 is present because the flux into the region of the complex is negative. It is useful to introduce the Heaviside (or step) function \( h[-f(q)] \) that is 1(0) inside (outside) the region of the complex; that is, \( f(q) = 0 \) defines a "dividing surface", with \( f(q) < 0 \) on the inside and \( f(q) > 0 \) on the outside. The flux is then given more generally in terms of it by

\[ F(p,r) = \delta(r-a)(p/m) \]  

(5a)

The second equality being true only for mass-scaled Cartesian coordinates.

Within the strong collision approximation the recombination probability \( P_r \) is the probability of a strong (i.e., deactivating)
collision sometime in the time interval \((0, \tau)\), where \(\tau = \tau(p_1, q_1)\) is the time at which the trajectory, which started inward from the dividing surface at \(t = 0\), returns to the dividing surface on its way out. This probability is:

\[
P_s(p_1, q_1; \omega) = 1 - e^{-\omega \tau(p_1, q_1)}
\]  

which can also be written as:

\[
P_s(p_1, q_1; \omega) = \int_0^\infty dt \omega e^{-\omega t} h(p_1, q_1; t)
\]  

because \(h(p_1, q_1, t) = h(-f(q(p_1, q_1; t)))\) is 1 for \(0 < t < \tau\) and 0 for \(t > \tau\). Also, with an integration parts eq 6b can also be written as:

\[
P_s(p_1, q_1; \omega) = \int_0^\infty dt \left(1 - e^{-\omega t}\right) F(p_1, q_1; t)
\]

where \(F(p_1, q_1, t)\) is the flux at time \(t\),

\[
F(p_1, q_1, t) = -\frac{d}{dt} h(-f(q(p_1, q_1; t)))
\]

\[
= \delta(f(q_1)) \frac{\partial f}{\partial q_1}/p/m
\]

with

\[q = q(p_1, q_1; t) \quad \text{and} \quad p = p(p_1, q_1; t)\]  

Using eq 6 in eq 4 thus allows the recombination rate to be written in several ways,

\[
k_{R} Q_{r} = -\int_0^\infty dt \omega e^{-\omega t} C_{fs}(t)
\]  

\[
k_{R} Q_{r} = -\int_0^\infty dt \left(1 - e^{-\omega t}\right) C_{f}(t)
\]

where \(C_{fs}(t)\) and \(C_{f}(t)\) are the flux–side and flux–flux correlation functions, respectively,

\[
C_{fs}(t) = (2\pi\hbar)^{-f} \int dp_1 \int dq_1 e^{-iH} F(p_1, q_1) h(p_1, q_1, t)
\]

\[
C_{f}(t) = (2\pi\hbar)^{-f} \int dp_1 \int dq_1 e^{-iH} F(p_1, q_1) F(p_1, q_1, t)
\]

which are related by

\[
C_{f}(t) = -\frac{d}{dt} C_{fs}(t)
\]

Finally, since

\[
\int_0^\infty dt C_{f}(t) = 0
\]

because here \(C_{f}(t)\) is the flux correlation function for a nonreactive process—eq 9b takes the simple form

\[
k_{R} Q_{r} = \int_0^\infty dt e^{-\omega t} C_{f}(t)
\]

It should be emphasized that the correlation functions \(C_{f}\) and \(C_{fs}\) themselves do not depend on \(\omega\); they are properties of the isolated \(A + B\) bimolecular collision dynamics.

**Quantum Mechanical Generalization**

The quantum mechanical generalization of the above formulas is transparent, following along the same lines for expressing quantum rate constants for chemical reactions in terms of time correlation functions; one simply replaces the correlation functions of eq 9 by their quantum mechanical counterparts, e.g.,

\[
C_{f}(t) = \text{tr}(\hat{F}e^{iH_{reac}t}) \hat{F}e^{-iH_{reac}t}
\]

where the Hamiltonian and flux operator, \(\hat{H}\) and \(\hat{F}\), are the usual ones, and \(t_c = t - i\hbar \beta/2\). (This quantum version of eqs 8a and 9a can be shown to be equivalent to the quantum rate expression given by Thiele.)

Proceeding further, the collision factor \(e^{-\omega t}\) in eq 11 can be combined with the time evolution operators in eq 12 to give the following expression for the recombination rate:

\[
k_{R} Q_{r} = \int_0^\infty dt \text{tr}(\hat{F}e^{iH_{reac}t} \hat{F}e^{-iH_{reac}t})
\]

where

\[
\hat{H}_{reac} = \hat{H} - \frac{i\hbar \omega}{2}
\]

That is, the collision frequency plays the role of an absorbing potential, a negative imaginary term added to the Hamiltonian; this corresponds physically to the loss of flux in the bimolecular \(A + B\) collision due to collisional stabilization of the complex. One can now follow the analysis of Seideman and Miller to obtain the following expression for the recombination rate:

\[
k_{R} Q_{r} = (2\pi\hbar)^{-f} \int dq_1 \int dq_2 h(q_1) (1 - h(q_2)) (\langle q_2 | \hat{G}_{\omega}(E) | q_1 \rangle)^2
\]

\[
N(E, \omega) = (\hbar \omega)^2 \text{tr} \left[ \hat{h} \hat{G}_{\omega}(E)^* (1 - \hat{h}) \hat{G}_{\omega}(E) \right]
\]

where \(\hat{G}_{\omega}(E) = \left(E + \frac{i\hbar \omega}{2} - \hat{H} \right)^{-1}\)

and \(h(q_1) = h(-f(q_1))\).

Although eq 15 is formally correct, in practical calculations one will likely wish to introduce an empirical absorbing potential function \(\varepsilon(q)\) in the region outside the complex (cf. Figure 1) to produce more rapid convergence. The complete absorbing potential will then be \((\hbar \omega/2)h(q) + \varepsilon(q)\), the first term producing absorption in the complex region (due to collisional stabilization) and the second term giving rise to absorption in the external region to enforce outgoing wave boundary conditions for the Green’s function. (The negative imaginary potential in the external region is actually \(\varepsilon(q) + 1 - h(q)\hbar \omega/2\), but the second term will essentially always be negligible compared to the first.) Equations 15 are then replaced by

\[
N(E, \omega) = 2\hbar \omega \text{tr} \left[ \hat{h} \hat{G}_{\omega}(E)^* \hat{G}_{\omega}(E) \right]
\]

\[
= 2\hbar \omega \int dq_1 \int dq_2 \varepsilon(q_1) \langle q_2 | \hat{G}_{\omega}(E) | q_1 \rangle^2
\]

with
Equations 11, 12, and 14–16 thus provide two ways to proceed, depending on which is more convenient: (1) one can calculate $C(t) = C(t,T)$ (of eq 12) for a given temperature $T$, and then eq 11 gives the recombination rate $k(T,\omega)$ for all $\omega$; or (2) one can calculate $N(E,\omega)$ (of eqs 15 or 16) for a given collision frequency $\omega$, and then eq 14 gives $k(T,\omega)$ for all temperatures $T$. (As the referee pointed out to me, the above equations also apply to the rate of radiative recombination if the collisional stabilization rate $\omega$ is replaced by the radiative rate, $k_r(q)$, where $t_r(q)$ is the lifetime for spontaneous emission, which is, in general, coordinate dependent. In this case, therefore, the absorbing potential in the complex region is $1/\tau_{t'}(q)$, and since it is now a coordinate-dependent operator one cannot bring it outside the trace as in eqs 15a and 16a but must follow the more general treatment in ref 11 and elsewhere.)

**Low-Pressure Limit**

The low-pressure ($\omega \to 0$) limit can be seen from eq 11 (or 8b) to be

$$\lim_{\omega \to 0} k_Q = \omega \int_0^\infty dt (-t) C(t)$$

which can be used to define the effective partition function for the complex $AB^*$,

$$Q_{AB^*} \equiv \int_0^\infty dt (-t) C(t)$$

so that the low-pressure recombination rate can be written in the standard form: \cite{12}

$$\lim_{\omega \to 0} k_r(T,\omega) = \frac{Q_{AB^*}}{Q_r} \omega K_{eq}(T)$$

(Equation 18 is reminiscent of an earlier classical expression of Bunker. \cite{13}) Another version of the effective partition function for $AB^*$ can be inferred from the $\omega \to 0$ limit of eqs 14 and 16a, namely,

$$Q_{AB^*} = \frac{1}{\tau_f} \int_{-\infty}^\infty dE e^{-\beta E} \text{tr}[\hat{H}(E)^* \hat{G}(E)]$$

with

$$\hat{G}(E) = (E + i\hbar - \hat{H})^{-1}$$

By examining the low-pressure limit of the classical expression eq 6a (used in eq 4),

$$\lim_{\omega \to 0} k_Q = -\omega(2\pi\hbar)^{-2} \int dp_1 \int dp_2 e^{-\beta H} F(p_1, q_1) \tau_r(p_1, q_1)$$

it is also possible to see how the present definition of the recombination rate compares to that of Smith, \cite{14} which has the “lifetime” $\tau_r(p_1, q_1)$ in eq 21 replaced by the time delay, $\tau - \tau_0$, where $\tau_0$ is the value of $\tau$ if $A$ and $B$ were noninteracting. Smith’s definition also takes the limit that the dividing surface is moved out to infinity. That is, Smith’s definition corresponds to the following modification of eq 21:

$$\tau \to \lim_{a \to \infty} (\tau - \tau_0)$$

There is also a quantum mechanical version\cite{14} of this time delay definition of the recombination rate.

If the contribution to the phase space integral in eq 21 (or the quantum mechanical trace) is dominated by long-lived collision complexes, then these two definitions of the recombination rate should be essentially equivalent. Smith’s definition has the advantage of being independent of the location of the dividing surface, but it also has unphysical features\cite{15} (e.g., negative contributions from “direct” scattering) that become more serious as the division between “complex” and “direct” scattering becomes less clear. I believe that the definition used above is more physically appropriate over the whole pressure range even though it does depend on the choice of the dividing surface.\cite{16} (For example, it is easy to see—e.g., from eqs 16 and 14—that the present definition gives a rate that is manifestly positive.)

**High-Pressure Limit**

In the high-pressure limit ($\omega \to \infty$) only the short-time part of the integral in eq 11 will contribute,

$$k_Q = \int_0^t dt C(t)$$

for small $\Delta t$, and this gives the transition state theory (TST) rate,\cite{5}

$$k_r = k_{TST}$$

In this limit the recombination rate is the incident flux through the dividing surface since all trajectories that enter the complex region are stabilized by collision.

**Simple Examples**

The classical RRKM recombination rate, eq 3, corresponds to the following flux correlation function:

$$C_r(t) = 2\delta(t) \sum_i e^{-\beta E_i} - \sum_i e^{-\beta E_i} k_i e^{-k_i t}$$

The first term is the short-time transition state theory contribution, and the second term is that of “recrossing flux”, i.e., trajectories (in a classical description) that dissociate back to $A + B$. (In the quantum version of the theory the classical TST $\delta$ function would be broadened somewhat, e.g., with a width of $\sim\hbar\beta$.) One can easily verify that

$$\int_0^\infty dt C_r(t) = 0$$

and that eq 11 gives the correct recombination rate,

$$k_r Q_r = \sum_i e^{-\beta E_i} k_i - \sum_i e^{-\beta E_i} k_i \omega (k_i + \omega)$$

(Note that the first term in eq 26a is the TST rate.)

The opposite limit, i.e., a short-lived complex, is illustrated by a one-dimensional free particle ($V(r) = 0, r > 0$). In this case the classical version of the flux correlation function is

$$C_r(t) = \frac{2\delta(t)}{2\pi\hbar\beta} - \frac{4\pi^2 m^2}{\hbar^2} e^{-\beta(2m\beta)^{1/2} t^2}$$

again showing the TST peak at $t = 0$ and negative recrossing behavior at longer time. Equation 11 cannot be evaluated
analytically in this case but can be expressed in the following form:

\[ k_i Q_{ir} = \frac{kT}{h} (2\pi\hbar)^{-1} \int_0^\infty dE e^{-2E} e^{-2mv/2\hbar} \]

(28)

where \( v = \sqrt{2\varepsilon/m} \) is the relative A-B velocity. Again, the first term, \( kT/\hbar = (2\pi\hbar\beta)^{-1} \), is the TST rate; the second term, the Boltzmann average of \( e^{-\omega r} \), \( \tau = 2a/v \) the time spent in the complex region \( 0 < r < a \). The low-pressure limit of eq 28 is of the form of eq 19, with

\[ Q_{AB} = \frac{E_0}{\pi \hbar^2} \int_0^\infty d\alpha \int_0^{\pi/2} d\theta e^{-Br^2/2m} \]

(29)

which is the classical partition function for the complex region \( (0,a) \). Equation 28 is also equivalent to eq 14 with the cumulative recombination probability given by

\[ N(E,\omega) = 1 - e^{-2mv/2\hbar} \]

(30)

Finally, the quantum mechanical result for the free particle example is most easily obtained from eq 15 since the free particle Green’s function is known analytically:

\[ \langle r| \hat{G}_e(E) |r' \rangle = -\frac{2m}{\hbar^2 k} \sin(kr_e) e^{-kr_e} \]

(31)

here with

\[ k = \sqrt{2m(E + \frac{\hbar\omega}{2})/\hbar^2} \equiv k_r + ik_i \]

The result given by eq 15 for \( N(E,\omega) \) is

\[ N(E,\omega) = \left( \frac{m\omega}{2\hbar} \right)^{2r} \left[ 1 - e^{-4k_r} - \frac{k_i}{k_r} e^{-2k_r} \sin(2k_r a) \right]/\left( k_r^2 + k_i^2 \right) \]

(32)

With appropriate approximations, i.e.,

\[ k_r \approx \sqrt{2mE/\hbar^2} \]

\[ k_i \approx \frac{\omega}{2} \sqrt{m/2E} \ll k_r \]

the classical result in eq 30 is recovered.

**Concluding Remarks**

Equations 11, 12, and 14–16 thus express the quantum recombination rate (within the strong collision approximation) in a form very similar to that recently developed for rate constants of chemical reactions. Methods that have been (and are still being!) developed for computing reactive flux correlation functions and cumulative reaction probabilities for chemical reactions\(^{11,17–24}\) should thus also be useful for calculating pressure-dependent recombination rates. Whether the time-dependent (eqs 11 and 12) or energy-dependent (eqs 14–16) version will be more useful will likely depend on the application.

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